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**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

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Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**





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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se referer à la description.)

Process for the preparation of an oxidic composition comprising a divalent and a trivalent metal

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09. 01. 2004

(95)

PROCESS FOR THE PREPARATION OF AN OXIDIC COMPOSITION  
COMPRISING A DIVALENT AND A TRIVALENT METAL

5 The present invention relates to a process for the preparation of an oxidic composition comprising a divalent and a trivalent metal, an oxidic composition obtainable by this process, and the use of this oxidic composition in FCC processes.

10 EP-A 0 554 968 (W.R. Grace and Co.) relates to a composition comprising a coprecipitated ternary oxide comprising 30-50 wt% MgO, 5-30 wt% La<sub>2</sub>O<sub>3</sub>, and 30-50 wt% Al<sub>2</sub>O<sub>3</sub>. The composition is used in FCC processes for the passivation of metals (V, Ni) and the control of SO<sub>x</sub> emissions.

15 This composition is prepared by co-precipitating a lanthanum salt, sodium aluminate, and magnesium nitrate with sodium hydroxide from an aqueous solution and aging the precipitate for 10-60 minutes at a pH of about 9.5 and 20-65°C, and filtering, washing and calcining the resulting precipitate at a temperature of 450-732°C. As will shown in Example 1 below, the aged co-precipitate comprises Mg-Al anionic clay.

20 The object of the present invention is to provide a process for the preparation of an oxidic composition with improved metal trap and de-SO<sub>x</sub> capacity.

The invention relates to a process for the preparation of an oxidic composition comprising a trivalent metal, a divalent metal and - calculated as oxide and  
25 based on the total composition - more than 18 wt% of one or more compounds selected from the group consisting of rare earth metal compounds, phosphorus compounds, and/or transition metal compounds, which process comprises the following steps:

30 a) preparing a precursor mixture comprising (i) a trivalent metal compound (compound 1), (ii) a divalent metal compound (compound 2), and (iii) a compound different from compound 1 and compound 2 and selected from

- the group consisting of rare earth metal compounds, phosphorus compounds, and transition metal compounds (compound 3),
- b) optionally aging the mixture, without anionic clay being formed,
  - c) drying the mixture, and
  - 5 d) calcining the product of step c).

As will be illustrated by the Examples below, this process results in the formation of oxidic compositions with improved metal trap and de-SO<sub>x</sub> capacity. Furthermore, the resulting oxidic compositions comprise individual, discrete  
10 oxide entities of divalent and trivalent metal oxide.

*Step a)*

The first step of the process involves the preparation of a physical mixture of a trivalent metal compound (compound 1), a divalent metal compound (compound  
15 2), and a compound selected from the group consisting of rare earth metal compounds, a phosphorus compounds, and/or a transition metal compounds (compound 3).

The physical mixture can be prepared in various ways. Compounds 1, 2, and 3 can be mixed as dry powders or in (aqueous) suspension thereby forming a  
20 suspension, a sol, or a gel. Compound 3 can also be added to the precursor mixture in the form of a compound 1 and/or a compound 2 that has been doped with compound 3.

It is noted that, in case the physical mixture is in an aqueous medium, at least one of compounds 1 and 2 is a water insoluble compound, such as an oxide,  
25 hydroxide, carbonate, or hydroxycarbonate.

The weight percentage of compound 1 in the precursor mixture is preferably 10 to 60 wt%, more preferably 20 to 40 wt%, and most preferably 25 to 35 wt%, calculated as oxides, and based on dry solids weight.

30 The weight percentage of compound 2 in the precursor mixture is preferably 10 to 60 wt%, more preferably 20 to 40 wt%, and most preferably 25 to 35 wt%, calculated as oxides, and based on dry solids weight.

The weight percentage of compound 3 in the precursor mixture is at least 18 wt%, preferably 18 to 60 wt%, more preferably 20 to 40 wt%, and most preferably 25 to 35 wt%, calculated as oxides, and based on dry solids weight.

- 5 The physical mixture may be milled before calcination, as dry powders or in suspension. Alternatively, or in addition to milling of the physical mixture, the compounds 1, 2, and 3 can be milled individually before forming the physical mixture. Equipment that can be used for milling include ball mills, high-shear mixers, colloid mixers, kneaders, electrical transducers that can introduce  
10 ultrasound waves into a suspension, and combinations thereof.

If the physical mixture is prepared in aqueous suspension, dispersing agents can be added to the suspension. Suitable dispersing agents include aluminium chlorohydrate, alumina gels, surfactants, phosphates (e.g. ammonium phosphate, aluminium phosphate), sugars, starches, polymers, gelling agents,  
15 swellable clays, etc. Acids or bases may also be added to the suspension.

#### *Compound 1*

Suitable trivalent metals include aluminium, gallium, indium, iron, chromium, vanadium, cobalt, manganese, cerium, niobium, nickel, lanthanum, and  
20 combinations thereof.

Aluminium compounds include aluminium alkoxide, aluminium oxides and hydroxides such as transition alumina, aluminium trihydrate (gibbsite, bayerite) and its thermally treated forms (including flash-calcined alumina), alumina sols, amorphous alumina, (pseudo)boehmite, aluminium-containing clays such as  
25 kaolin, sepiolite, modified clays such as metakaolin or acid-treated bentonite, and aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate, sodium aluminate, and aluminium sulphate. With the preparation method according to the invention it is also possible to use coarser grades of aluminium trihydrate such as BOC (Bauxite Ore Concentrate) or bauxite.

30 Iron compounds include iron ores such as goethite (FeOOH), akaganeite, bernalite, ferrosilite, ferrihydrite, lepidocrocite, limonite, maghemite, magnetite, hematite, and wustite, synthetic iron products such as synthetic iron oxides and



hydroxides, and iron salts such as iron nitrate, iron chloride, iron sulphate, iron oxalate, iron carbonate, and iron hydroxycarbonate.

Suitable gallium, indium, iron, chromium, vanadium, cobalt, cerium, niobium, lanthanum and manganese compounds are the respective oxides, hydroxides,  
5 carbonates, nitrates, chlorides, chlorohydrates, and alkoxides.

Also mixtures of the above-mentioned trivalent metal compounds can be used, or additive-containing trivalent metal compounds, such as trivalent metal compounds doped with compound 3. Such additive-containing metal compounds are prepared by treatment of a trivalent metal compound in the  
10 presence of an additive (e.g. compound 3). Examples of additive-containing trivalent metal compounds are additive-containing quasi-crystalline boehmite according to WO 01/12551 and WO 01/12553 and additive-containing micro-crystalline boehmite according to WO 01/12552.

#### 15 *Compound 2*

Suitable divalent metal compounds include magnesium, zinc, nickel, copper, iron, cobalt, manganese, calcium, barium, strontium, and combinations thereof.

Suitable magnesium compounds are oxides or hydroxides such as MgO and Mg(OH)<sub>2</sub>, hydromagnesite, magnesium carbonate, magnesium hydroxy  
20 carbonate, magnesium bicarbonate, magnesium salts such as magnesium acetate, magnesium formate, magnesium hydroxy acetate, magnesium nitrate, and magnesium chloride, and magnesium-containing clays such as dolomite, saponite, and sepiolite. Suitable zinc, nickel, copper, iron, cobalt, manganese, calcium, and barium compounds are the respective oxides, hydroxides,  
25 carbonates, hydroxycarbonates, nitrates, and chlorides.

Also mixtures of the above-mentioned divalent metal compounds can be used, or additive-containing divalent metal compounds, e.g. divalent metal compounds doped with compound 3. Such additive-containing metal compounds are prepared by treatment of a divalent metal compound with a  
30 suitable additive (e.g. compound 3). An example of an additive-containing divalent metal compound is additive-containing brucite. . . . .

*Compound 3*

Suitable rare earth metals include Ce, La, and mixtures thereof. These metals are preferably present in the precursor mixture in the form of their nitrates, chlorides, sulphates, oxides, hydroxides, etc. Also bastnaesite can be used as a suitable mixture of rare earth metals.

Suitable transition metals include Cu, Zn, Ni, Co, Fe, Mn, Cr, Mo, W, V, and mixtures thereof. These metals are preferably present in the precursor mixture in the form of their nitrates, chlorides, sulphates, oxides, hydroxides, etc.

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Suitable phosphorus compounds include phosphoric acid and its salts such as ammonium dihydrogen phosphate and diammonium hydrogen phosphate, ammonium hypophosphate, ammonium orthophosphate, ammonium dihydrogen orthophosphate, ammonium hydrogen orthophosphate, triammonium phosphate, sodium pyrophosphate, phosphines, and phosphites. Suitable phosphorus-containing compounds also include derivatives of groups represented by  $PX_3$ ,  $RPX_2$ ,  $R_2PX$ ,  $R_1P$ ,  $R_3P=O$ ,  $RPO_2$ ,  $RPO(OX)_2$ ,  $PO(OX)_3$ ,  $R_2P(O)OX$ ,  $RP(OX)_2$ ,  $ROP(OX)_2$ , and  $(RO)_2POP(OR)_2$ , wherein R is an alkyl or phenyl radical and X is hydrogen, R or halide. These compounds include primary,  $RPH_2$ , secondary,  $R_2PH$ , and tertiary,  $R_3P$ , phosphines such as butyl phosphine; tertiary phosphine oxides,  $R_3PO$ , such as tributyl phosphine; primary,  $RP(O)(OX)_2$ , and secondary,  $R_2P(O)OX$ , phosphonic acids such as benzene phosphonic acid; esters of the phosphonic acids such as diethyl phosphonate,  $(RO)_2P(O)H$ , dialkyl phosphinates,  $(RO)P(O)R_2$ ; phosphinous acids,  $R_2POX$ , such as diethylphosphinous acid, primary,  $(RO)P(OX)_2$ , secondary,  $(RO)_2POX$ , and tertiary,  $(RO)_3P$ , phosphites; and esters thereof such as monopropyl ester, alkylalkyl phosphinites,  $(RO)P_2$ , and dialkyl phosphonite,  $(RO)_2PR$  esters. Examples of phosphite esters include trimethyl phosphite, triethyl phosphite, diisopropyl phosphite, butyl phosphite; and pyrophosphites such as tetrapyrophosphite. The alkyl groups in the mentioned compounds preferably contain 1 to 4 carbon atoms. Other suitable phosphorus-containing compounds include phosphorus halides such as phosphorus

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trichloride, bromide, and iodide, alkyl phosphorodichloridites, (RO)PCl<sub>2</sub>, dialkyl phosphorochloridites, (RO)<sub>2</sub>PCl, alkyl phosphonochloridates, (RO)(R)P(O)Cl, and dialkyl phosphinochloridates, R<sub>2</sub>P(O)Cl.

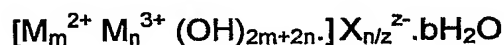
The advantage of using organic phosphates is that the organic group may increase the porosity of the final product after calcining.

*Step b)*

The physical mixture can be aged, provided that no anionic clay is formed.

10 Anionic clays - also called hydrotalcite-like materials or layered double hydroxides - are materials having a crystal structure consisting of positively charged layers built up of specific combinations of divalent and trivalent metal hydroxides between which there are anions and water molecules, according to the formula

15



wherein M<sup>2+</sup> is a divalent metal, M<sup>3+</sup> is a trivalent metal, and X is an anion with valency z. m and n have a value such that m/n=1 to 10, preferably 1 to 6, more preferably 2 to 4, and most preferably close to 3, and b has a value in the range of from 0 to 10, generally a value of 2 to 6 and often a value of about 4.

Hydrotalcite is an example of a naturally occurring anionic clay wherein Mg is the divalent metal, Al is the trivalent metal, and carbonate is the predominant anion present. Meixnerite is an anionic clay wherein Mg is the divalent metal, Al is the trivalent metal, and hydroxyl is the predominant anion present.

If formation of anionic clay is prevented, calcination (step d) results in the formation of compositions comprising individual, discrete oxide entities of divalent metal oxide and trivalent metal oxide. In case of Mg as the divalent and Al as the trivalent metal, this would result in the formation of both acidic (Al<sub>2</sub>O<sub>3</sub>) and basic (MgO) sites being accessible to molecules to be adsorbed or to be converted in catalytic reactions.

Consequently, this enables the entrapment of both acidic compounds (e.g. S-heterocycles,  $\text{SO}_x$ , V-containing compounds) and basic compounds (e.g. N-heterocycles, Ni-containing compounds).

- 5 Formation of anionic clay during aging can be prevented by aging for a short time period, i.e. a time period which, given the specific aging conditions, does not result in anionic clay formation.

Aging conditions which influence the rate of anionic clay formation are the temperature (the higher, the faster the reaction), the pH (the higher, the faster  
10 the reaction), the type and the particle size of compounds 1 and 2 (larger particles react slower than smaller ones), and the presence of additives that inhibit anionic clay formation (e.g. vanadium, sulphate)

*Step c)*

- 15 The precursor mixture, either aged or not, is dried to an extent that makes the material suitable for calcination. Drying can be performed by any method, such as spray-drying, flash-drying, flash-calcining, and air drying.

*Step d)*

- 20 The dried product is calcined at a temperature in the range of 200-800°C, more preferably 300-700°C, and most preferably 350-600°C. Calcination is conducted for 0.25-25 hours, preferably 1-8 hours, and most preferably 2-6 hours. All commercial types of calciners can be used, such as fixed bed or rotating calciners.

- 25 Calcination can be performed in various atmospheres, e.g. in air, oxygen, inert atmosphere (e.g.  $\text{N}_2$ ), steam, or mixtures thereof.

Preferably, the calcination conditions are chosen such that spinel formation is prevented, as spinel is not very active as metal trap.

- It is possible to add an additive during calcination of the physical mixture,  
30 provided that the calciner has sufficient mixing capability and can be effectively used as mixer as well as calciner.

*Use of the oxidic composition*

The oxidic composition obtainable from the process according to the invention can suitably be used in or as a catalyst or catalyst additive in a hydrocarbon conversion, purification, or synthesis process, particularly in the oil refining industry and Fischer-Tropsch processes. Examples of processes where these compositions can suitably be used are catalytic cracking, hydrogenation, dehydrogenation, hydrocracking, hydroprocessing (hydrodenitrogenation, hydrodesulfurisation, hydrodemetallisation), polymerisation, steam reforming, base-catalysed reactions, gas-to-liquid conversions (e.g. Fischer-Tropsch), and the reduction of SO<sub>x</sub> and NO<sub>x</sub> emissions.

In particular, they are very suitable for use in FCC processes for the reduction of SO<sub>x</sub> and NO<sub>x</sub> emissions, reduction of the sulfur and nitrogen content of fuels like gasoline and diesel, and for entrapment of metals like V and Ni.

The product obtainable from the process according to the invention can be added to the FCC unit as such, or in a composition containing conventional FCC catalyst ingredients, such as matrix or filler materials (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite, etcetera), and molecular sieve material (e.g. zeolite Y, ZSM-5, etcetera).

20

## FIGURES

Figure 1 shows a powder X-ray diffraction (PXRD) pattern of an aged co-precipitate according to EP 0 554 968.

Figure 2 shows a powder X-ray diffraction (PXRD) pattern of the material of Figure 1 after calcination.

Figure 3 shows the powder X-ray diffraction (PXRD) pattern of MgO.

25

## EXAMPLES

Comparative Example 1

5 Example 1 of EP 0 554 968 was reworked. A powder X-ray diffraction (PXRD) pattern was made of the aged co-precipitate. See Figure 1. The main lines present can be identified as the interlayer spacing 8.74 Å (20.63° 2-theta using Cu K-alpha radiation), indicative of a hydrotalcite that contains nitrate as the charge balancing anion.

10 Calcination of this material at 704°C for 2 hours resulted in a material having a PXRD pattern with peaks at about 43° and 62° 2-theta (Figure 2; measured with Cu K-alpha radiation). Comparison with Figure 3 – a PXRD pattern of MgO – shows that this calcined material contains a crystalline MgO phase.



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## CLAIMS

(95)

1. Process for the preparation of an oxidic composition comprising a trivalent metal, a divalent metal and - calculated as oxide and based on the total composition – more than 18 wt% of one or more compounds selected from the group consisting of rare earth metal compounds, phosphorus compounds, and transition metal compounds, which process comprises the following steps:
  - a) preparing a precursor mixture comprising (i) a compound 1 being a trivalent metal compound, (ii) a compound 2 being a divalent metal compound, and (iii) a compound 3 being different from compounds 1 and 2 and being selected from the group consisting of rare earth metal compounds, phosphorus compounds, and transition metal compounds,
  - b) optionally aging the mixture, without anionic clay being formed,
  - c) drying the mixture, and
  - d) calcining the product of step c).
2. Process according to claim 1 wherein the divalent metal of compound 2 is selected from the group consisting of Mg, Ca, Ba, Zn, Ni, Cu, Co, Fe, Mn, and mixtures thereof.
3. Process according to claim 2 wherein the divalent metal is Mg.
4. Process according to claim 3 wherein the magnesium compound is selected from the group consisting of magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium hydroxyl carbonate, magnesium salts, and mixtures thereof.
5. Process according to any one of the preceding claims wherein the trivalent metal of compound 1 is selected from the group consisting of Al, Ga, Fe, Cr and mixtures thereof.



6. Process according to claim 5 wherein the trivalent metal is Al and wherein the aluminium compound is selected from the group consisting of aluminium oxides, aluminium trihydrate, thermally treated aluminium trihydrate, gel alumina, boehmite, aluminium salts, and mixtures thereof.
- 5
7. Process according to claim 5 wherein the trivalent metal is Fe and wherein the iron compound is selected from the group consisting of iron oxides, iron hydroxides, and iron salts.
- 10
8. Process according to any one of the preceding claims wherein compound 3 is a compound comprising a metal selected from the group consisting of Cu, Zn, Ni, Co, Fe, Mn, Cr, Mo, W, V, Ce, La, and mixtures thereof.
- 15
9. Process according to any one of the preceding claims wherein compound 3 is introduced into the precursor mixture by using a compound 1 that has been doped with compound 3 and/or a compound 2 that has been doped with compound 3.
- 20
10. Process according to any one of the preceding claims wherein compound 3 is present in the composition in a total amount of 18 to 60 wt%, calculated as oxide and based on the total composition.
- 25
11. Oxidic composition obtainable by the process according to any one of the preceding claims.
12. Catalyst composition or catalyst additive composition comprising the oxidic composition according to claim 11.
- 30
13. Catalyst composition according to claim 12 comprising a matrix or filler and a molecular sieve.

14. Use of the oxidic composition of claim 11 or the catalyst composition of claim 13 or 14 as metal trap in FCC, for the reduction of SO<sub>x</sub> and/or NO<sub>x</sub> from flue gasses, the reduction of the sulfur-content in fuels, the reduction of the nitrogen content in fuels, gas-to-liquid conversion, hydrogenation, hydrodesulfurisation, hydrodenitrogenation, or a demetallisation process.



09.01.2004

## ABSTRACT

(95)

- Process for the preparation of an oxidic composition comprising a trivalent metal, a divalent metal and - calculated as oxide and based on the total composition – more than 18 wt% of one or more compounds selected from the group consisting of rare earth metal compounds, phosphorus compounds, and transition metal compounds, which process comprises the following steps: (a) preparing a precursor mixture comprising (i) a compound 1 being a trivalent metal compound, (ii) a compound 2 being a divalent metal compound, and (iii) a compound 3 being different from compounds 1 and 2 and being selected from the group consisting of rare earth metal compounds, phosphorus compounds, and transition metal compounds, (b) optionally aging the mixture, without anionic clay being formed, (c) drying the mixture, and (d) calcining the product of step c).
- The resulting oxidic composition is suitable as a metal trap and SO<sub>x</sub> sorbent FCC processes.



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(95)

Figure 1/3

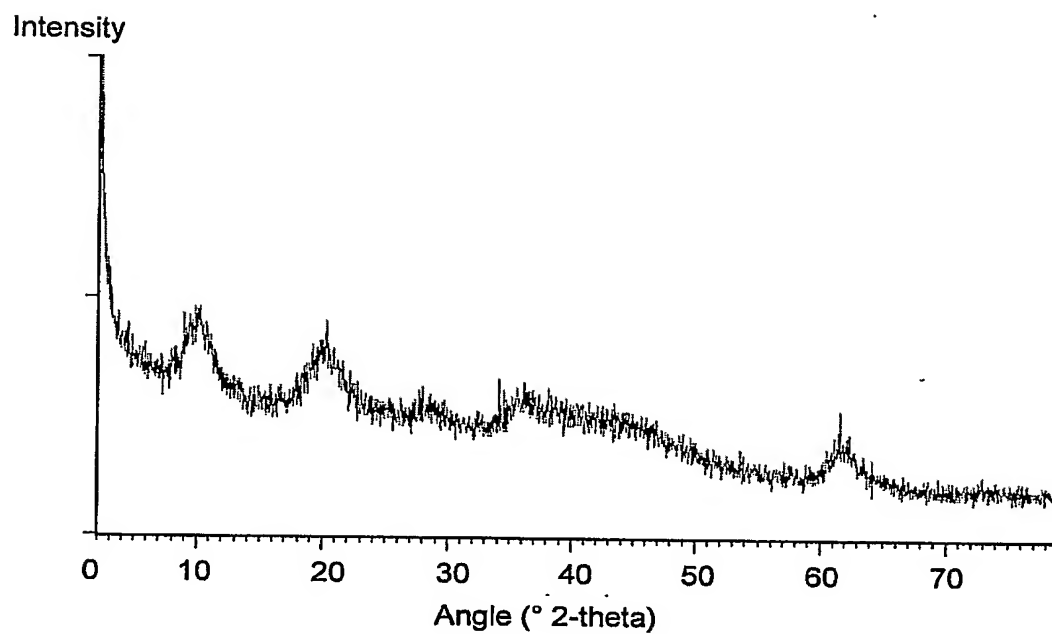


Figure 2/3

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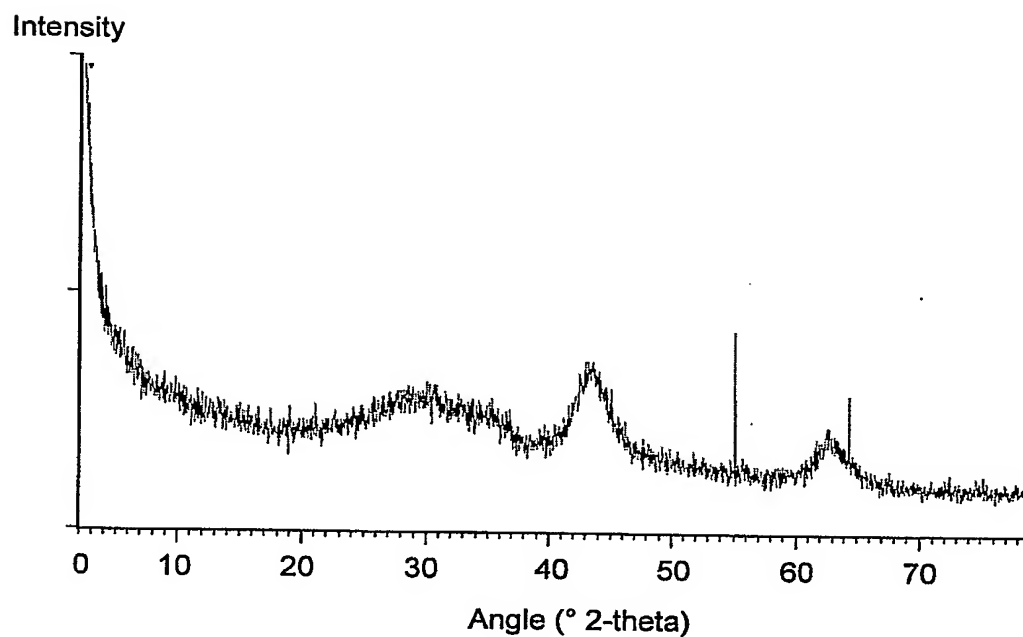


Figure  
3/3

